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Seasonal characteristics and sources of carbonaceous components and elements of PM_{10} (2010–2019) in Delhi, India

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Abstract
In this study we present the seasonal chemical characteristics and potential sources of PM_{10} at an urban location of Delhi, India during 2010-2019. The concentrations of carbonaceous aerosols [organic carbon (OC), elemental carbon (EC), water soluble organic carbon (WSOC) and water insoluble organic carbon (WIOC)] and elements (Al, Fe, Ti, Cu, Zn, Mn, Pb, Cr, F, Cl, Br, P, S, K, As, Na, Mg, Ca, B, Ni, Mo, V, Sr, Zr and Rb) in PM_{10} were estimated to explore their possible sources. The annual average concentration (2010–2019) of PM_{10} was computed as 227 ± 97 μg m^{-3} with a range of 34-734 μg m^{-3}. The total carbonaceous aerosols in PM_{10} was accounted for 22.5% of PM_{10} mass concentration, whereas elements contribution to PM_{10} was estimated to be 17% of PM_{10}. The statistical analysis of OC *vs.* EC and OC *vs.* WSOC of PM_{10} reveals their common sources (biomass burning and/or fossil fuel combustion) during all the seasons. Enrichment factors (EFs) of the elements and the relationship of Al with other crustal metals (Fe, Ca, Mg and Ti) of PM_{10} indicates the abundance of mineral dust over Delhi. Principal component analysis (PCA) extracted the five major sources [industrial emission (IE), biomass burning + fossil fuel combustion (BB + FFC), soil dust, vehicular emissions (VE) and sodium and magnesium salts (SMS)] of PM_{10} in Delhi, India. Back trajectory and cluster analysis of airmass parcel indicate that the pollutants approaching to Delhi are mainly from Pakistan, IGP region, Arabian Sea and Bay of Bengal.

Keywords $PM_{2.5}$ · PM_{10} · OC · EC · WSOC · Elements · PCA

1 Introduction

A megacity Delhi is considered to be one of the most polluted city in the world, bearing the choking level particulate matter (PM) over the city. The impact of PM on climate and human health have become a subject of major concern for the scientific community

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and public powers all around the world in recent years (IPCC 2013). Carbonaceous aerosols (CAs) are the major fractions of PM in the atmosphere and have significant role in visibility degradation, alteration of atmospheric chemistry and the Earth's radiative balance (Lim and Turpin 2002; Hansen et al. 2005; Bond et al. 2013). Various toxic gases, organics and hydrocarbons are produced during the combustion process/emissions of CAs and therefore affect the respiratory as well as cardiovascular system of the human (Lighty et al. 2000; Pope et al. 2009a, b). Both primary and secondary organic aerosols significantly control of physical and chemical properties of aerosols (Kanakidou et al. 2005) and influenced the formation cloud condensation nuclei (CCN), whereas EC absorb solar radiation and contribute for radiative change (Bond et al. 2013). PM consists of organics (OC, EC, and other components), mineral/crustal/soil dust, metals, non-metals, inorganic pollutants, sea salts and relative exuberance of these species are highly variable both spatially and temporally (Ram et al. 2011; Jain et al. 2017).

Generally, the elements linked with the PM are non-volatile in nature and remain unaffected even though they go for regional as well as long-range transportation (Morawska and Zhang 2002). Some of the transition/toxic metals (like Fe, Cu, Mn, Zn, Ni, Cr, As, Pb, Hg) which are coming from the various sources into the ambient air have acute toxic and mutagenic effects on human health, when inhaled at higher concentrations. Elements like Fe, Al, Si, Ca and Ti are also available in the fine and coarse mode PM is originated from mineral dust/crustal dust (Sharma et al. 2014a). Soluble K in PM mostly originated from biomass burning, however, it is also considered to be dust in PM (Viana et al. 2008), whereas Cl originated from sea salt is also considered from coal burning in aerosols (Pant and Harrison 2012). Therefore, quantification and identification of chemical species and sources of PM is essential to explore the appropriate mitigation option to improve the ambient air quality, human health and climate (Ramana et al. 2010; Cao et al. 2006; Bond et al. 2013; Pope et al. 2009a, b; Ramgolam et al. 2009; Sharma et al. 2018a, b).

Several studies conducted in past on carbonaceous aerosols, inorganic aerosols and elements of particulate matter and their potential sources in urban (Ram and Sarin, 2011; Mandal et al. 2014; Sharma et al. 2016; Gupta et al. 2017; 2018; Gadi et al. 2019; Shivani et al. 2019; Jain et al. 2020a, b), rural, remote (Begam et al. 2017) as well as high altitude atmosphere (Kumar and Attri, 2016; Sarkar et al. 2017; Kaushal et al. 2018; Sharma et al. 2020a,b) of India on seasonal basis and restricted to a year long data sets, but limited study has been conducted on long-term basis over the IGP region of India. The atmospheric carbonaceous aerosols and elements in PM bear immense importance from the perspective of climate change and bio-geochemical cycles over the region (Sharma et al. 2016). Hence, considering the importance of atmospheric carbonaceous species and elements of PM_{10} in urban area, a long-term observations has been carried out at megacity Delhi. In the present study, the concentrations of carbonaceous species (OC, EC, WSOC. WIOC, POC and SOC) and elements (Al, Fe, Ti, Cu, Zn, Mn, Cr, Ni, Mo, Cl, P, S, K, Zr, Pb, Na, Mg, Ca, and B) of PM_{10} are estimated during 2010–2019 to explore the possible sources of PM_{10} over Delhi.

2 Materials and methods

2.1 Description of study site

Delhi is situated in northern part of India and it is considered to be one of the most polluted megacity in the world with annual average PM_{10} concentration approaching

more than 10-times the WHO (world health organization guideline: 25 μg m^{-3}). Delhi has currently 31.2 million population (WRP 2021) and over ~ 11 million registered vehicles (Statistical Abstract of Delhi 2020). PM_{10} samples were collected periodically at CSIR-National Physical Laboratory (CSIR-NPL), New Delhi (28°38′N, 77°10′E; 218 m amsl) during January, 2010, to December, 2019. The study site represents an urban background surrounded by nearby traffice and Indian Agricultural Research Institute (IARI) in north and south-west direction (Fig. 1). A year long meteorology of Delhi is divided into four (as per India Metrological Department (IMD), New Delhi classification) distinct seasons: winter (January - February), summer (March - May), monsoon (June - September) and post-monsoon (October - December). Winter months are chilly (temperature: ~ 2 °C) and observe intense fog and haze. Summers are generally very hot and dry (temperature: 47 °C) and observe frequent dust storms (soil and mineral dust). A detailed description of sampling site is discussed in our previous publication (Sharma et al. 2018a).

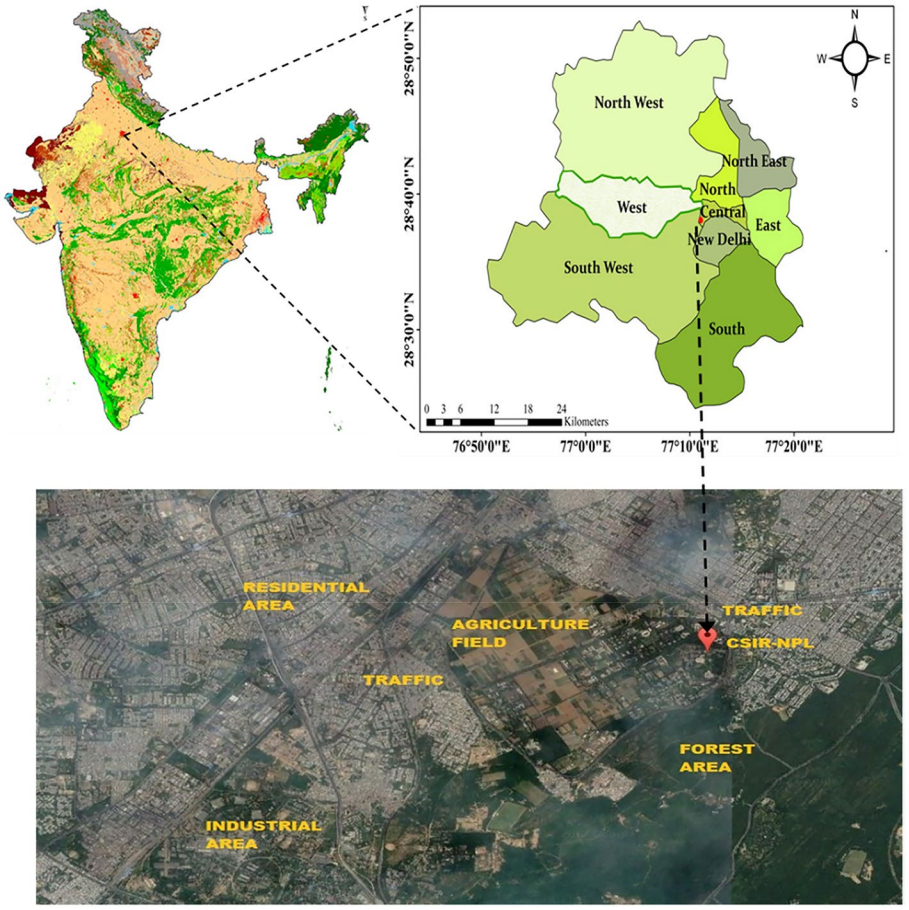

Fig. 1 Map of the study site in Delhi (*Source:* Google maps)

2.2 Sample collection and analysis

Coarse mode particulate matter (PM_{10}) samples ($n=674$) were collected periodically (2 samples in a week) on pre-combusted (at 550 °C) Pallflex tissue quartz filters using Respirable Dust Sampler (flow rate:1.2 m^3 $min^{-1} \pm 2\%$), for 24 h from January 2010-December 2019 (except January-December 2012). The details of the instrument used for PM_{10} sample collections are depicted in Table S1 (in supplementary information). The sampler was installed at the rooftop of CSIR-NPL, New Delhi at 10 m height (above the ground level: AGL). The gravimetric mass (in µg) of PM_{10} was estimated by the difference between final and initial weight (weighing balance: M/s. Sartorius, resolution: ± 10 µg) of the filter. PM_{10} concentrations (in µg m^{-3}) was further computed by dividing the PM_{10} mass to the total volume of air passed during 24 h (sampling period). Prior to chemical analysis the samples were stored in deep freezer at −20 °C.

OC and EC concentrations of PM_{10} were analyzed by Thermal/Optical Carbon Analyzer (Model: DRI 2001A) applying IMPROVE-A Protocol (Chow et al. 2004). Thermal/Optical Carbon Analyzer is working on the preferential oxidation of OC and EC at different temperatures (140, 280, 480, 580, 740 and 840 °C). The instrument analyzes the OC fractions (OC1, OC2, OC3 and OC4), pyrolyzed carbon fraction (OP) and EC fractions (EC1, EC2 and EC3), respectively in helium and helium + oxygen environment (Chow et al. 2004; Sharma et al. 2014a, b). A proper punch of ~ 0.536 cm^2 area of the PM_{10} filter was cut and analyzed in triplicate along with field blank filters. The standard calibration for peak area verification was performed daily using 5% CH_4 + balance helium gas. Calibration of the OC/EC analyzer was performed by 4.8% of CO_2 + balance He gas along with known amounts of KHP (potassium hydrogen phthalate) and sucrose solution. In the present case, repeatability error of OC and EC analysis were estimated as 3–7% ($n=3$). To account for the unmeasured H, O, N, and S in organic compounds, a conversion factor (or multiplier) is used to transform OC to OM ($OM = f \times OC$). The f multipliers of 1.4 and 1.8 are depending on the extent of OM oxidation and secondary organic aerosols (SOA) formation. The values of f vary from 1.2 for fresh aerosol in urban areas (Chow et al. 2004) to 2.6 for aged aerosol (Robinson et al. 2007). In the present case, TCA of PM_{10} is computed as OM + EC [$(OM = 1.8 \times OC) + EC$] (Rengarajan et al. 2007; Srinivas and Sarin 2014). The detailed analytical and calibration procedures of Thermal/Optical Carbon Analyzer is described in our previous publication (Sharma et al. 2014a, b).

The 10 ml filtered extract of PM_{10} samples were analyzed to estimate the concentrations of WSOC and WIOC using a TOC analyzer working on catalytically-aided combustion oxidation method (Model: Shimadzu TOC-L CPH/CPN, Japan). Briefly, sample extracts were injected and sprayed onto high temperature platinum catalyst at 680◦ C to convert total carbon to CO_2 and measured by NDIR detector. Consecutively, inorganic carbon in the water extract was determined after acidification of another aliquot of the sample of P^H 2 with 25% phosphoric acid and measuring the evolved CO_2. The NDIR detector response for inorganic carbon was calibrated with a Na_2CO_3 standard. The water-soluble organic carbon was assessed from the difference between the total carbon and the inorganic carbon. The repeatability of WSOC was estimated to be 3–10% based on triplicate analysis of each filter. The detail, analytical procedures is described in Rai et al. (2020a).

The concentrations of elements i.e., Al, Fe, Ti, Cu, Zn, Mn, Cr, Ni, Mo, Cl, P, S, K, Zr, Pb, Na, Mg, Ca, and B etc., in PM_{10} are analyzed (with repeatability errors 5–10%)

using Wavelength Dispersive X-ray Fluorescence Spectrometer (WD-XRF). The analysis of major and trace elements were carried out by a non-destructive method of quantitative elemental analysis using Wavelength Dispersive X-Ray Fluorescence (ZSX Primus, Rigaku, Japan). Measurement of elements were taken under standard reference conditions (vacuum condition, 36 ºC temperature and 2.4 kW tube rating). The parameter method was employed in the quantitative analysis given in ZSX software package of WD-XRF. The instrument WD-XRF was calibrated periodically using micro-matter thin-film standards (Watson et al. 1999). PM_{10} samples were analyzed in triplicate and for these major and trace elements. The detail analytical procedures is available in Jain et al. (2020a, b).

2.3 Estimation of POC and SOC

The seasonal concentrations of primary organic carbon (POC) in PM_{10} samples are calculated using minimum OC/EC ratio of each season (for winter:1.26, summer:1.48, monsoon:1.58 and post-monsoon:1.55). The concentration of POC is computed using the following equation (Castro et al. 1999),

$$POC = [OC/EC]_{min} \times [EC] \quad (1)$$

Secondary organic carbon (SOC) of PM_{10} is estimated as the difference between OC and POC (SOC = OC–POC).

2.4 Enrichment Factors (EFs)

Crustal EFs referes the origin of the elements (either anthropogenic or natural) and their abundance in the ambient particulates (Amato et al. 2016). EFs of the elements present in atmosphereic PM_{10} samples are computed (Taylor and McLennan, 1995) as:

$$\mathrm{EF} = \frac{\mathrm{Esample/Xsample}}{\mathrm{Ecrust/Xsample}} \quad (2)$$

where,

E_{sample} = element (E) concentration.

X_{sample} = reference element (X) concentration.

E_{crust} = element (E) concentration in upper continental crust.

X_{crust} = reference element (X) concentration in upper continental crust.

Aluminium (Al) is used as the reference element in this study (Khilare and Sarkar 2012; Sharma et al. 2014a, b).

2.4.1 Principal component analysis (PCA)

PCA was applied on chemical constituents of PM_{10} to identify the potential sources contributing to PM_{10} concentration. It uses orthogonal decomposition to identify individual groups of components which are then tied to variables by loading factors (Viana et al. 2008). The detail processes, mathematical equations and hypothesis of PCA are available in various literatures (Song et al. 2006; Jain et al 2021).

3 Results and discussion

3.1 Variations in concentrations of chemical species of PM_{10}

3.1.1 Variation in PM_{10} concentration

Figures 2-3 shows the temporal variation in mass concentrations of PM_{10} and its chemical components monitored during Januray 2010 to December 2019 (including annual trend in Fig. S2). The annual average concentration (9-year average) of PM_{10} was estimated as 227 ± 92 μg m^{-3} (range: 33—733 μg m^{-3}) with annual average maxima (279 ± 99 μg m^{-3}) in 2016 and annual average minima (189 ± 59 μg m^{-3}) in 2010. The year-wise annual concentrations of PM_{10}, OC, EC, WSOC, WIOC, POC and SOC from Januray 2010 to December 2019 are depicted in Table 1 (including annual trend of OC, EC and WSOC in Fig. S2). The maximum monthly concentration (pooled estimate of 9 years) of PM_{10} was noted in colder month December (346 ± 42 μg m^{-3}) and the minimum monthly average concentration of PM_{10} was observed in September (127 ± 42 μg m^{-3} μg m^{-3}) during monsoon month. The monthly average concentration of PM_{10} are shown in Fig. 3. The highest seasonal average concentration of PM_{10} (304 ± 92 μg m^{-3}) were found during post-monsoon seasons followed by winter (271 ± 95 μg m^{-3}), summer (221 ± 81 μg m^{-3}) and monsoon (181 ± 85 μg m^{-3}) seasons (Table 2). Sharma et al. (2014a, b) (213 μg m^{-3}), Mandal et al. (2014) (285 μg m^{-3}), Jain et al. (2019) (250 μg m^{-3}), Kulshrestha et al. (2009) (219 μg m^{-3}), Perrino et al. (2011) (183 μg m^{-3}) and Tiwari et al. (2013) (161 μg m^{-3}) are also reported the similar concentration

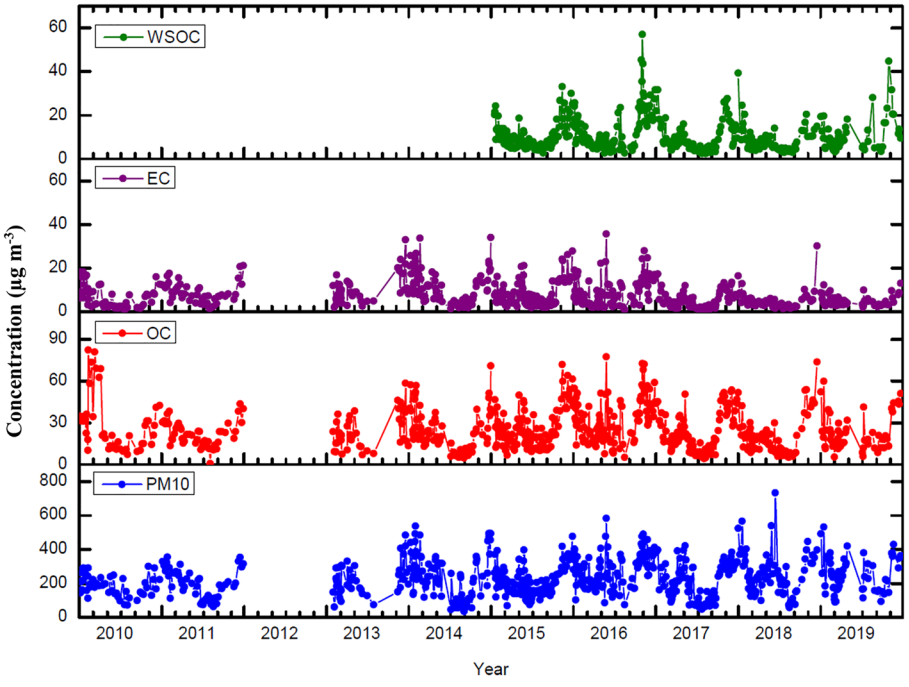

Fig. 2 Temporal variation in concentrations of PM_{10} and carbonaceous species (OC, EC and WSOC) of PM_{10} over Delhi during 2010–2019

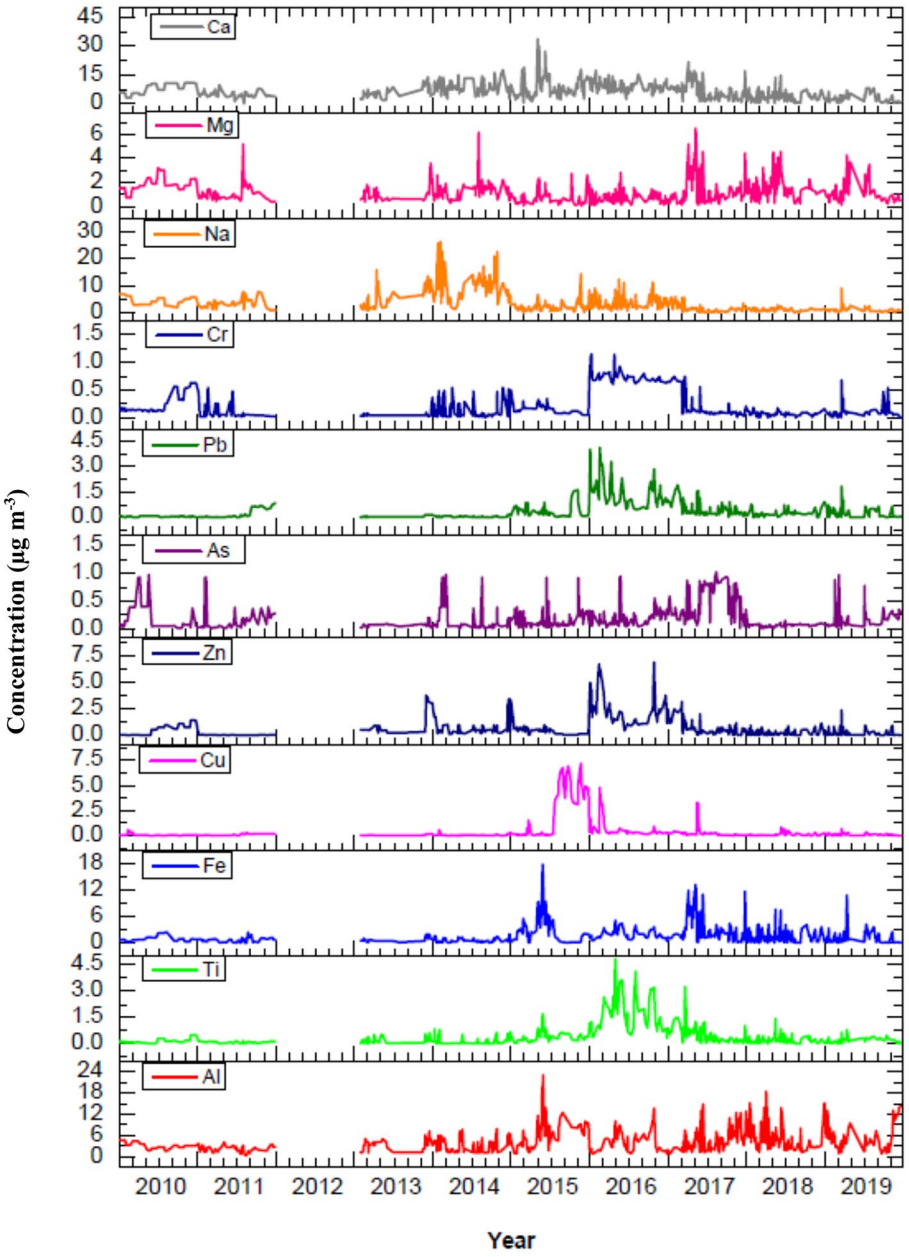

Fig. 3 Temporal variation in concentration of elements present in PM_{10} over Delhi during 2010–2019

of PM_{10} over Delhi. All these studies breached the threshold limit (24 h average: 100 µg m^{-3} and annual average: 60 µg m^{-3}) of National Ambient Air Quality Standards (NAAQS) of India. Highest PM_{10} concentration during post-monsoon season (October-December) were mainly attributed to the firework display during Diwali festival and crop residue burning

Table 1 Annual mean concentrations of PM_{10} and its carbonaceous species (OC, EC, WSOC, WIOC, POC and SOC) in Delhi

Year	PM_{10}	OC	EC	WSOC	WIOC	POC	SOC	OC/EC
	(μg m^{-3})							
2010	189 ± 59	29.2 ± 19.7	6.9 ± 5.1	na	na	11.5 ± 7.2	17.6 ± 15.0	4.2
2011	200 ± 85	22.1 ± 8.6	8.6 ± 4.7	na	na	16.3 ± 6.2	5.9 ± 3.2	2.6
2013	225 ± 93	23.2 ± 12.2	10.7 ± 6.6	na	na	17.4 ± 6.8	5.8 ± 4.9	2.2
2014	234 ± 98	22.5 ± 14.5	10.6 ± 7.4	na	na	13.4 ± 5.9	9.2 ± 6.4	2.1
2015	209 ± 81	25.4 ± 13.4	7.8 ± 5.5	10.1 ± 5.9	15.3 ± 6.2	10.5 ± 6.9	14.9 ± 7.4	3.3
2016	279 ± 99	32.7 ± 15.7	9.4 ± 6.6	13.5 ± 9.8	19.2 ± 8.7	20.4 ± 9.7	12.3 ± 7.3	3.5
2017	207 ± 98	23.1 ± 13.9	5.2 ± 3.7	9.6 ± 6.5	13.5 ± 9.5	9.6 ± 5.2	13.5 ± 8.5	4.4
2018	253 ± 95	20.0 ± 13.3	4.9 ± 3.8	8.6 ± 5.6	11.4 ± 7.2	7.7 ± 4.9	12.3 ± 9.5	4.1
2019	250 ± 86	22.1 ± 12.5	4.9 ± 2.4	10.6 ± 7.7	11.5 ± 8.1	7.3 ± 4.7	14.8 ± 9.8	4.5
Mean	227 ± 97	24.5 ± 13.8	7.7 ± 5.1	10.5 ± 7.1	11.5 ± 8.1	12.7 ± 6.3	11.8 ± 8.5	3.4
	(33.6 – 733.7)	(0.72 – 82.5)	(0.81 – 35.6)	(2.3 –57.0)	(2.1 – 35.2)	(3.1 –19.2)	(2.6 – 41.6)	(1.5 –10.3)

± Standard deviation ($n = 674$, from 2010–2019); values in parentheses are ranges; na: not analyzed

activities in the agricultural activities along with meteorological conditions like high relative humidity, low wind speed and low boundary layer height resulted in accumulation of PM_{10} mass generated from these activities in the lower surface (Shivani et al. 2019). Higher concentration of pollutants during winter season (January–February) could be attributed to the prevailing meteorological conditions i.e. low temperature, stable atmosphere (cool air causes inversions that stagnate the air and trap pollution close to the ground) and low wind speed. While during summer season (March–May) higher windspeed along with high mixing height results in dispersion of pollutants. However, frequent dust storms during summer season increase the PM concentration in the region. On contrary, rainfall during monsoon season scavenged off the atmospheric particles leading to their lower concentration (Sharma et al. 2016).

3.1.2 Variation in OC, EC and WSOC of PM_{10}

Temporal variations in OC, EC and WSOC concentrations of PM_{10} during study period are shown in Fig. 2. The total annual average (9 years) concentrations of OC, EC, WSOC, WIOC, POC and SOC of PM_{10} were 24.5 ± 13.8 μg m^{-3}, 7.7 ± 5.1 μg m^{-3}, 10.5 ± 7.1 μg m^{-3}; 11.5 ± 8.1 μg m^{-3}, 12.7 ± 6.3 μg m^{-3} and 11.8 ± 8.5 μg m^{-3}, respectively. Figure 3 shows the monthly average concentrations of OC, EC and WSOC in PM_{10} during the entire study period in Delhi (pooled estimate of 9 years). Highest monthly average OC in PM_{10} (48.1 ± 13.8 μg m^{-3}) was found in December (post-monsoon/cold season), whereas monthly average minima of OC in PM_{10} (12.5 ± 8.3 μg m^{-3}) was found in August (monsoon). Similar monthly average maxima and minima of EC (in PM_{10}) was recorded in December (15.7 ± 6.9 μg m^{-3}) and August (3.4 ± 2.4 μg m^{-3}) of post-monsoon and monsoon, respectively (Fig. 3). Highest monthly average concentration of WSOC concentration in PM_{10} (20.6 ± 6.4 μg m^{-3}; 50% of OC) was recorded in November (post-monsoon) may be due to the influence of stubble burning nearby northern states of India (Punjab, Haryana and western Uttar

Table 2 Seasonal variations in mass concentrations of carbonaceous species (OC, EC, WSOC, POC, SOC and TCA) and elements of PM_{10} (μg m^{-3}) in Delhi

Components	Seasons			
	Winter ($n=148$)	Summer ($n=203$)	Monsoon ($n=184$)	Post-Monsoon ($n=139$)
PM_{10}	271 ± 95	221 ± 81	151 ± 85	304 ± 92
OC	29.1 ± 13.2	22.3 ± 11.5	14.1 ± 8.2	38.0 ± 14.4
EC	9.5 ± 5.5	6.6 ± 4.7	4.0 ± 2.5	12.1 ± 6.6
WSOC	12.7 ± 6.3	7.8 ± 2.7	5.8 ± 3.2	18.4 ± 8.6
WIOC	16.4 ± 8.3	14.5 ± 9.0	8.3 ± 7.9	19.6 ± 10.8
POC	15.2 ± 9.1	10.6 ± 8.5	6.7 ± 5.1	20.5 ± 11.8
SOC	13.9 ± 10.6	11.7 ± 8.8	7.4 ± 5.0	17.5 ± 10.4
TCA	62.0 ± 27.8	46.6 ± 23.9	29.4 ± 16.9	80.6 ± 31.1
OC/EC	3.7 ± 2.8	3.4 ± 1.9	3.5 ± 1.6	3.7 ± 1.9
WSOC/OC	0.44 ± 0.27	0.35 ± 0.23	0.41 ± 0.29	0.48 ± 0.39
POC/OC	0.52 ± 0.41	0.48 ± 0.32	0.47 ± 0.32	0.54 ± 0.41
SOC/OC	0.48 ± 0.32	0.52 ± 0.35	0.53 ± 0.33	0.46 ± 0.28
TCA/PM_{10}	0.23 ± 0.12	0.21 ± 0.09	0.19 ± 0.29	0.27 ± 0.13
Na	4.42 ± 4.19	2.68 ± 2.26	3.43 ± 2.70	4.25 ± 3.95
Mg	0.88 ± 0.49	1.18 ± 1.05	1.17 ± 0.93	1.03 ± 0.69
Ca	6.23 ± 3.70	7.38 ± 5.41	6.65 ± 4.33	7.03 ± 3.93
K	4.74 ± 4.11	3.78 ± 3.36	2.46 ± 2.08	6.72 ± 6.34
Al	3.54 ± 2.53	4.28 ± 3.25	4.14 ± 3.37	5.20 ± 3.47
Fe	1.13 ± 1.01	2.50 ± 2.04	1.86 ± 1.77	1.26 ± 1.07
Ti	0.33 ± 0.32	0.68 ± 0.64	0.45 ± 0.42	0.55 ± 0.46
As	0.17 ± 0.16	0.16 ± 0.13	0.22 ± 0.19	0.23 ± 0.20
Cu	0.26 ± 0.25	0.22 ± 0.21	0.64 ± 0.56	0.82 ± 0.65
Zn	1.01 ± 1.00	0.70 ± 0.62	0.41 ± 0.29	1.07 ± 1.05
Mn	0.16 ± 0.12	0.23 ± 0.22	0.19 ± 0.14	0.18 ± 0.15
Pb	0.57 ± 0.42	0.45 ± 0.39	0.28 ± 0.22	0.52 ± 0.43
Cr	0.27 ± 0.19	0.26 ± 0.17	0.18 ± 0.12	0.25 ± 0.23
F	0.83 ± 0.75	0.84 ± 0.61	0.66 ± 0.51	0.75 ± 0.65
Cl	13.54 ± 11.49	7.91 ± 7.82	5.84 ± 5.37	11.14 ± 10.21
Br	0.23 ± 0.21	0.14 ± 0.11	0.11 ± 0.09	0.24 ± 0.22
P	0.23 ± 0.15	0.26 ± 0.17	0.16 ± 0.12	0.20 ± 0.17
S	4.01 ± 2.10	2.95 ± 1.48	2.72 ± 1.78	4.64 ± 2.77

± Standard deviation

[a] Significantly different ($p < 0.05$)

Pradesh of IGP) and minima in August (5.2 ± 3.1 μg m^{-3}). The seasonal average concentrations of OC, EC, WSOC, WIOC, POC, SOC TCA and their weight ratios are summarized in Table 2. Highest seasonal average concentration of OC was recorded in post-monsoon (38.0 ± 14.4 μg m^{-3}) and minimum seasonal average of OC was recorded during monsoon (14.1 ± 8.2 μg m^{-3}). Similarly, seasonal average maxima and minima of EC were recorded in post-monsoon (12.1 ± 6.6 μg m^{-3}) and monsoon

(4.0 ± 2.5 μg m^{-3}) seasons. Average WSOC concentration was also recorded highest during post-monsoon saeson (18.4 ± 8.6 μg m^{-3}) and minimum in monsoon season (5.8 ± 3.2 μg m^{-3}).

Total annual average concentration of TCA contributes 22.5% of PM_{10} (54.7 ± 24.5 μg m^{-3}) mass concentration. The highest TCA in PM_{10} was recorded in post-monsoon (26.5% of PM_{10}) season followed by winter (22.9% of PM_{10}), summer (21.1% of PM_{10}) and monsoon (19.4% of PM_{10}) seasons. The annual average concentration of POC of PM_{10} was 12.7 ± 6.3 μg m^{-3} (52.1% of OC; range: 33–76% of OC) and SOC was 11.8 ± 8.5 μg m^{-3} (48.2% of OC; range: 25–67% of OC) during entire study period. The seasonal contribution of POC and SOC were ranging from 48–54% and 48–42% of OC, respectively. Jain et al. (2017) reported almost similar percentage contributions of OC (10% of PM_{10}), EC (5% of PM_{10}) and TCA (23% of PM_{10}) of PM_{10} at Delhi, whereas Mandal et al. (2014) reported higher percentage contributions of OC (32.8% of PM_{10}), EC (9.5% of PM_{10}) and TCA (61.8% of PM_{10}) of PM_{10} in an industrial area of Delhi. Ram et al. (2011) also reported 22% OC and 3% EC of PM_{10} at an urban site of Kanpur in IGP of India during 2009. Monthly as well as seasonal variations in concentrations of PM_{10}, OC, EC and WSOC may be due to the source strength and prevailing meteorological conditions at the measurement site of Delhi. The changes in mixing height of the boundary layer during the various seasons may also influence the higher concentration of PM_{10} and its carbonaceous species (Salma et al. 2004; Begum et al. 2011). It is noteworthy that apart from stable atmosphere and lowered boundary layer height, the particulates emitted from crop residue burning in the states of Punjab and Haryana (a popular after harvesting practise performed by farmers during the months of October and November), get transported and advected towards Delhi region (Gupta et al. 2018; Shivani et al. 2019). This is the major cause of loading of carbonaceous aerosols during post-monsoon season over the sampling region. Other scientific studies also exhibit similar seasonal pattern of OC and EC concentration in Delhi (Sharma et al. 2014a, b; Sharma et al. 2016; Jain et al. 2017; Gupta et al. 2018; Gadi et al. 2019; Shivani et al. 2019).

Figure 3b shows the monthly average OC/EC and WSOC/OC ratios of PM_{10} at Delhi, whereas the seasonal relationship between OC & EC and WSOC & OC of PM_{10} are depicted in Fig. S1 (see the supplementary information). The seasonal average OC/EC ratio of PM_{10} was 3.7 ± 2.8, 3.4 ± 1.9, 3.5 ± 1.6 and 3.7 ± 1.9 during winter, summer, monsoon and post-monsoon, respectively whereas the seasonal average WSOC/OC ratio of PM_{10} was reported as 0.44, 0.35, 0.41 and 0.48 during winter, summer, monsoon and post-monsoon, respectively. Banoo et al. (2020) reported the similar seasonal OC/EC ratios (3.4, 3.5, 4.0 and 3.9 during winter, summer, monsoon and post-monsoon, respectively) over National Capital Region (NCR) of Delhi wheraes WSOC/OC ratios as 0.55, 0.47, 0.57 and 0.60 during winter, summer, monsoon and post-monsoon, respectively. It is to be noted that the poor solubility of organics emitted from the combustion of the fossil fuels (diesel, petrol etc.) the WSOC/OC values for vehicular emissions are low (< 0.20) as compared to biomass burning (0.20–0.80). Therefore, biomass burning emissions have higher solubility in water than fossil fuel combustion (Rengarajan et al. 2007). In this study, significant positive correlation between OC *vs.* EC ($r^2 = 0.68$, $r^2 = 0.73$, $r^2 = 0.82$ and $r^2 = 0.69$ at $p < 0.05$ during winter, summer, monsoon and post-monsoon seasons, respectively) of PM_{10} has been observed during all the seasons (Table S2; in supplementary information), which is indicative of their common sources (Rengarajan et al. 2007; Ram and Sarin 2011). The positive correlation of K (a tracer of biomass) with Na, Ca and Mg of PM_{10} during all the seasons (except post-monsoon) demonstrate the abundance of soil dust contributed by

soluble organic sources to PM_{10} at study site (Tables S3-S6; in supplementary information). It is considered that the soil suspension, fuel combustion (Urban et al. 2012), and formation of secondary water soluble organic aerosols (Lim et al. 2010) are also some other sources of WSOC in the sampling site of Delhi.

3.1.3 Concentration of elements in PM_{10}

During the entire sampling period (2010–2019) 18 common elements (Al, Fe, Ti, Cu, Zn, Mn, Pb, Cr, F, Cl, Br, P, S, K, As, Na, Mg, and Ca) were extracted in PM_{10} (B, Ni, Mo, V, Sr, Zr and Rb are also traced in few samples ranges from 0–0.09 μg m^{-3}) using X-RF technique. The annual and seasonal statistical summary of elements recorded in PM_{10} samples is tabulated in Table 2. Higher concentrations of Ca, Na, Cl, K, Al, and Fe were observed during all the seasons with seasonal variability. The temporal variation in concentration elements present in PM_{10} samples are depicted in Fig. 4; whereas monthly average concentrations of elements of PM_{10} are shown in Fig. 5. Highest average contribution of elements to PM_{10} are accounted for 20.9% (of PM_{10}) during monsoon season followed by summer (16.5% PM_{10}), winter (15.7% of PM_{10}) and post-monsoon seasons (15.2% of PM_{10}). The similar contribution of elements to the PM_{10} over Delhi is also reported by Rai et al. (2020a, b; 2021).

Figure 6 depicts the seasonal enrichment factors (EFs) of the elements (Al, Fe, Ti, Cu, Zn, Mn, Pb, Cr, F, Cl, Br, P, S, K, As, Na, Mg, and Ca) available in PM_{10} samples. Al, Fe, Ti, K, Mg, and Ca in PM_{10} have recorded low EFs (< 5) for all the seasons, which indicate that, elements mostly arrived from crustal/soil sources (Sharma et al. 2014a, b; Saxena et al. 2017). The element like Cu, Zn, Ni, Pb, Cr, Mo and B have higher EFs (> 10) in both $PM_{2.5}$ and PM_{10} and therefore are likely of anthropogenic origin. The higher the EF of Cr, Ni, Pb and Zn of PM_{10} were also attributed to industrial emission (IE) sources. Generally Cu, Mn, Zn, Ni, Cd, Fe, Mo, S and Cr used as a marker for IE in India (Shridhar et al. 2010).

In this study, Fe/Al ratio is 0.40 (winter: 0.32; summer: 0.58; monsoon: 0.45 and post-monsoon: 0.24), which indicates the dominant source of mineral/crustal dust at the study site. The average Ca/Al ratio (1.62) indicates (in winter: 1.78; summer: 1.72; monsoon: 1.61 and post-monsoon: 1.35) that PM_{10} over the Delhi region is rich in Ca dust as compared to average continental crust. Sarin et al. (1979) had reported that the Fe/Al ratio in north Indian plains ranged from 0.55 to 0.63. Kumar and Sarin (2009) reported Fe/Al ratio as 0.59 for $PM_{2.5–10}$ at a remote high altitude sampling site (Manora Peak, Nainital: ~ 1951 m above the mean sea level) of western India. McLennan, (2001) recorded the average Ca/Al ratio as 1.07 in PM_{10} whereas, the corresponding ratio in the upper continental crust is 0.38. Correlation matrix of Al with Fe, Ca, Mg and Ti of PM_{10} during all the seasons are also indicated the abundance of mineral/soil dust in Delhi (Table S3-S6; in supplementary information).

3.2 Possible sources and source regions

3.2.1 Sources of PM_{10}

Principal component analysis (PCA) has been performed with 23 chemical species of PM_{10} (OC, EC, WSOC, SOC, POC, Al, Fe, Ti, Cu, Zn, Mn, Pb, Cr, F, Cl, Br, P, S, K, As, Na, Mg, and Ca) to extract the factor loading to PM_{10}. Seasonal factor profiles (9 year long data sets) for the possible sources of PM_{10} was extracted using PCA are summarized in Table S7a-d (in supplementary information). On the basis of the factor loading PCA

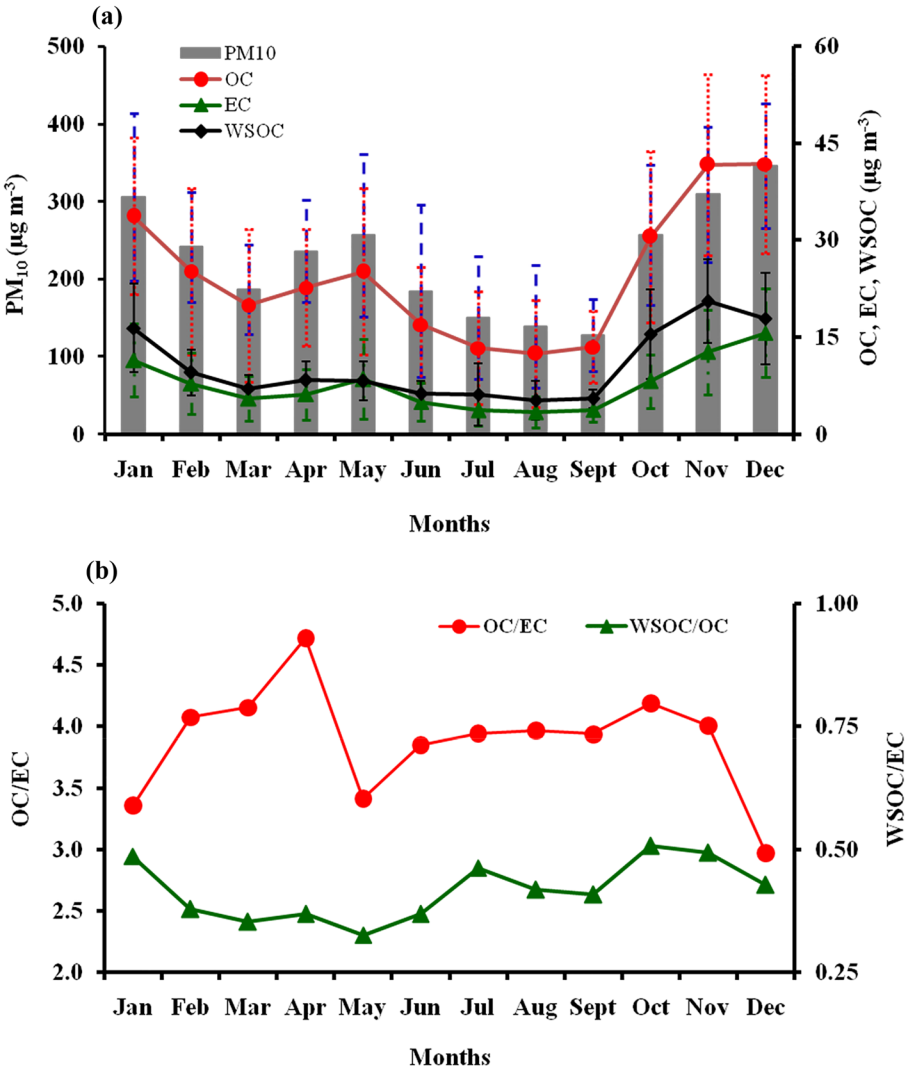

Fig. 4 Average monthly variation in (**a**) concentrations of PM_{10}, OC, EC, WSOC and (**b**) OC/EC and WSOC/OC ratios of PM_{10} over Delhi during 2010–2019

resolved the five common sources [industrial emissions (IE), biomass burning + fossil fuel combustion (BB + FFC), crustal/soil dust (SD), vehicular emissions (VE) and sodium and magnesium salts (SMS)] of PM_{10} during winter, summer, monsoon (extracted four sources) and post-monsoon seasons at an urban site of Delhi.

Source 1: During winter season the first source of PM_{10} is characterized as industrial emissions (IE) due to higher loading of Cu, Zn, Mn, Cr, S, Fe and Pb in aerosol samples (Table S7a). These elements (Cu, Zn, Ni, Cr and Mo) are generally originated from the small to medial scale industries, metal processing industries, industrial effluents and coal fired thermal power plants (Gupta et al. 2007; Jain et al. 2019). During summer,

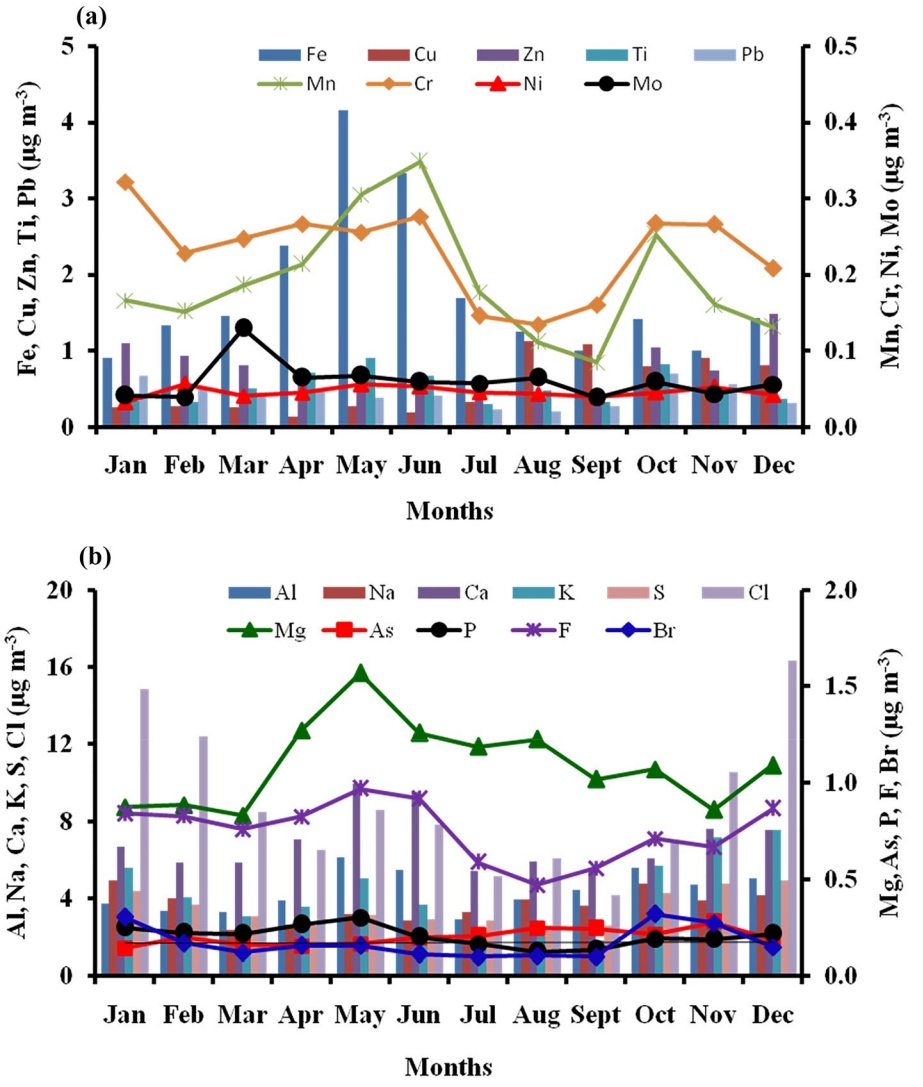

Fig. 5 Average monthly variation in concentrations of (**a**) transition/toxic elements (**b**) other elements available in PM_{10} over Delhi during 2010–2019

IE was also extracted as a factor 1 of PM_{10} with 27.4% of variance (Table S7b) whereas during monsoon and post monsoon seasons IE was extracted as factor 2 (Table S7c-d); in supplementary information).

Source 2: The second factor of represents the BB + FFC, characterized (18.8% of the variance during winter and 20.5% of the variance during summer) by highly loaded with OC, EC, WSOC, SOC, POC, K, and Cl. K^+ and Levoglucoson are considered BB (cow dung, crop residue, fuel wood, and wildfires, etc.) marker, whereas presence of Cl in the factor reveals the wood and coal burning (Pant and Harrison 2012). WSOC/OC and OC/EC ratios also evidence the BB + FFC as a one of the sources of PM_{10} at the observational

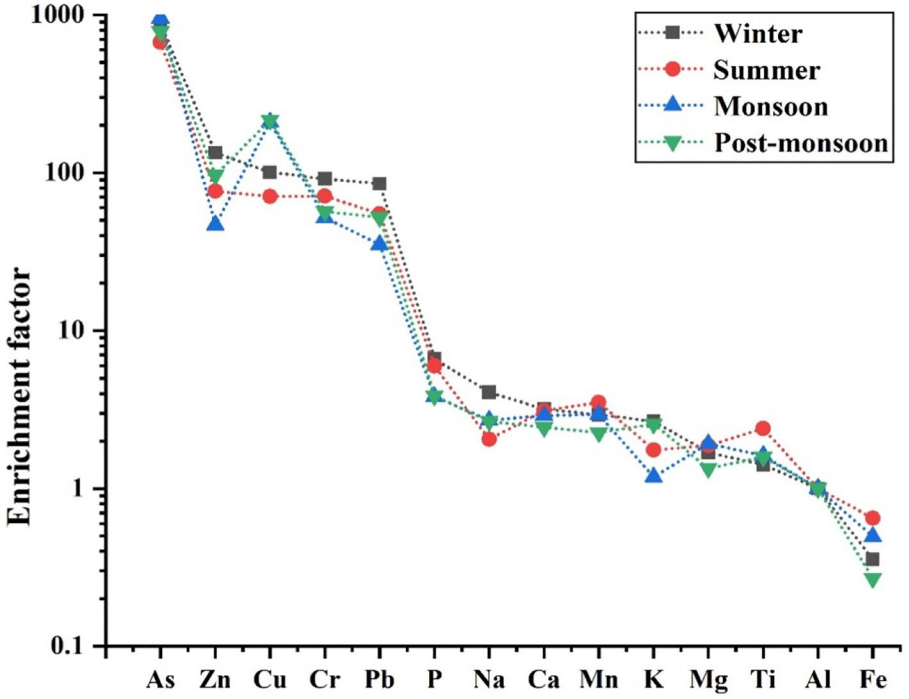

Fig. 6 Enrichment factors (EFs) of elements present in PM_{10} during winter, summer (pre-monsoon), monsoon and post-monsoon seasons

site of Delhi (Banoo et al. 2020). Factor 1 was extracted as source of BB + FFC during monsoon and post-monsoon seasons with 30.3% and 24.6% of the variance, respectively (Table S7c-d) in supplementary information).

Source 3: The third factor of PM_{10} represented by high loading (12.5%, 11.1%, 13.3% and 12.2% of the variance during winter, summer, monsoon and post-monsoon seasons, respectively) of crustal elements like, Al, Ti, Fe, Ca, Mg, K and Na which inferred the source as crustal/soil/road dust during winter, summer, monsoon and post-monsoon seasons (Begum et al. 2011; Sharma et al. 2014a; Jain et al. 2020b). The abundance of these elements at the study site as crustal origin is also confirmed by EFs (Fig. 5) as well as positive correlations of Al with Ca, Mg and Ti (Table S1-S8). This factor of $PM_{2.5}$ was resolved as crustal/soil dust by high loading of Al, Ti, Fe, Ca, Mg, K and Na (17.6% of the variance of factor loading) (Table S7a-d). The EFs of these elements are also suggesting the crustal origin the elements at sampling site (Fig. 6) of Delhi as well as the positive correlations of Al with Ca, Mg, Fe and Ti.

Source 4: The fourth factor of PM_{10} constitutes the vehicular emissions (VE) with the dominant presence of EC, OC, Zn, Mn, and Cr indicates (with 9.4%, 9.9%, 10.7% and 9.3% of the variance during winter, summer, monsoon and post-monsoon seasons, respectively) the emission derived from road side vehicles (Pant and Harrison 2012; Jain et al. 2020b). Since, EC and OC are majorily emitted from the combustion sources, so these

components are considered as important tracers for VE globally (Yin et al. 2010; Beum et al. 2011). Zn and Mn are used as marker of brake and tire wear, two stroke engine emissions (Zn as fuel additive), heavy duty diesel truck emission (Mn as fuel additive) (Kothai et al. 2008; Sharma et al. 2014a). VE is inferred to be one of the major sources of aerosols (Sharma et al. 2020b) at in urban sites of Delhi region may due to the great influence of public and private vehicles (light and heavy vehicles) (Jain et al. 2020a, b).

Source 5: Fifth source is resolved as sodium and magnesium salt (SMS) due to high factor loading of Na and Mg (Choi et al. 2013). Even though, Na, Mg, and Cl are used as markers for sea salt or marine aerosols (Pant and Harrison 2012) however the sampling site neither is and nor surrounded by coastal region, hence it would be more relevant to refer this source as sodium and magnesium salt (Jain et al. 2019). However, long-range transportation of the pollutants from the Arabian Sea and Bay of Bengal (Fig. 7) to the sampling site may be considered as sea salt as a source in stead of SMS. The contribution of SMS was extracted by PCA during all the seasons with < 8% of variance excluding monsoon season (where combined source was extracted i.e., SMS). During monsoon season heavy rainfall and winds flowing from Arabian Sea and Bay of Bengal (Fig. 7) contribute to SMS/sea salt loading in the sampling region (Jain et al. 2017).

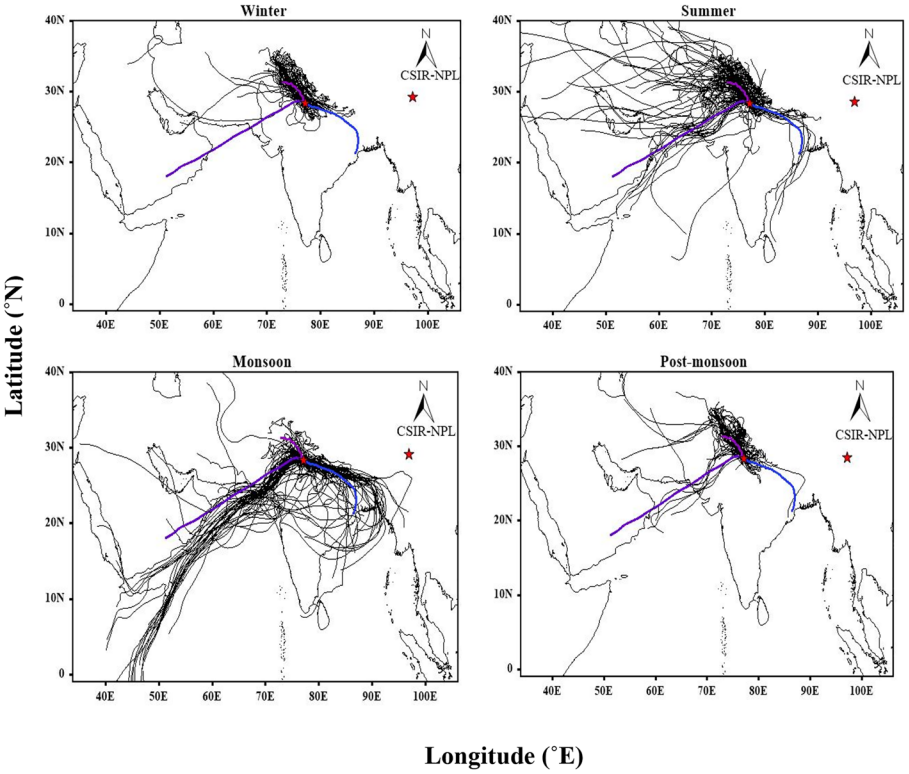

Fig. 7 120 h air mass HYSPLIT back trajectories with cluster analysis during, winter, summer (pre-monsoon), monsoon and post-monsoon seasons over Delhi from 2010–2019

3.2.2 Air mass backward trajectory/source region

To explore the transport pathway of PM_{10} at the observational site of Delhi, 120 h air-mass back trajectory was computed using the HYSPLIT model (Draxler and Rolph 2003) at an altitude of 500 m AGL (Fig. 7). During winter, air parcels approaching to sampling site is mainly from the continental region of IGP, India [northern part of India (Punjab, Haryana) and eastern part (Uttar Pradesh)]. During summer, pollutants reaching to receptor site from the northern India (Punjab, Haryana, eastern part of Uttar Pradesh) including Pakistan (continental region) as well as from marine region (Arabian sea through Gujarat and Rajasthan). During monsoon season, the air mass also approaching to sampling site from Arabian sea (through Gujarat and Rajasthan) and Bay of Bengal (through eastern IGP of India). Jain et al. (2021) reported the similar air parcels towards the Delhi during all the seasons over Delhi during 2013–2016.

4 Conclusions

The annual and seasonal characteristics of carbonaceous aerosols and elements in PM_{10} were estimated during 2010-2019 to explore the prominent sources of PM_{10} in megacity Delhi, India. During the entire study period, the average concentration of PM_{10} was recorded as 227 ± 97 μg m^{-3} with non-significant increasing annual trend. The seasonal average total CAs in PM_{10} was accounted for 26.5%; 22.9%; 21.1% and 19.4%; of PM_{10}, during post-monsoon, winter, summer and monsoon seasons, respectively. The annual average (pooled average of 9-year data) contribution of elements to PM_{10} is accounted for 17% of PM_{10} (during monsoon: 20.9%; summer: 16.5%; winter: 15.7% and post-monsoon: 15.2%). Significant positive linear relationship between OC & EC; and OC & WSOC (OC/EC and WSOC/OC ratios) indicate the BB + FFC are one of the major sources of carbonaceous aerosols at the urban site of Delhi. EFs of the elements indicates the abundance of mineral/soil dust in the megacity Delhi during all the seasons. PCA resolved the five common sources (IE, BB + FFC, crustal/SD, VE and SMS) of PM_{10} over the region. 120-h HYSPLIT back trajectory air parcels indicate that the pollutants approaching to Delhi are mainly from continental [Pakistan, IGP region (Punjab, Haryana and Uttar Pradesh)] as well as marine region (Arabian Sea and Bay of Bengal).

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Authors' contributions Conception and design of the study were planned by SKS; Data collection and analysis were performed by SKS, RB, TKM; the first draft was written by SKS. Data interpretation was carried out by SKS, TKM and RB. All the authors read and approved the final manuscript.

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Data availability The datasets developed during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of interests The authors declare that they have no conflict of interest.

References

Amato, F., Alastuey, A., Karanasiou, A., Lucarelli, F., Nava, S., Calzolai, G., Severi, M., Becagli, S., Vorne, L.G., Colombi, C., Alves, C., Custódio, D., Nunes, T., Cerqueira, M., Pio, C., Eleftheriadis, K., Diapouli, E., Reche, C., Minguillón, M.C., Manousakas, M.I., Maggos, T., Vratolis, S., Harrison, R.M., Querol, X.: IRUSE-LIFE. Atmos. Chem Phys **16**, 3289–3309 (2016)

Banoo, R., Sharma, S.K., Gadi, R., Gupta, R., Mandal, T.K.: Seasonal variation of carbonaceous species of PM_{10} over urban sites of National Capital Region of India. Aerosol Sci Engin **4**(2), 111–123 (2020)

Begam, G.R., Vachaspati, C.V., AhammedYN, K.K.R., Reddy, R.R., Sharma, S.K., Saxena, M., Mandal, T.K.: Seasonal characteristics of water soluble inorganic ions and carbonaceous aerosols in total suspended particulate matter at a rural semi-arid site, Kadapa (India). Environ Sci Poll Res **24**(2), 1719–1734 (2017)

Begum, B.A., Hossain, A., Saroar, G., Biswas, S.K., Nasiruddin, M., Nahar, N., Chowdury, Z., Hopke, P.K.: Sources of carbonaceous materials in the airborne particulate matter of Dhaka. Asian J Atmos Environ **5**(4), 237–246 (2011)

Bond, T.C., Doherty, S.J., Fahey, D.W., Forster, P.M., Berntsen, T., DeAngelo, B.J., Flanner, M.G., Ghan, S., Kärcher, B., Koch, D., Kinne, S.: Bounding the role of black carbon in the climate system: A scientific assessment. J Geophy Res **118**(11), 5380–5552 (2013)

Cao, J.J., Chow, J.C., Lee, S.C., Li, Y., Chen, S.W., An, Z.S., Fung, K., Watson, J.G., Zhu, C.S., Liu, S.X.: Characterization and source apportionment of atmospheric organic and elemental carbon during fall and winter of 2003 in Xi'an, China. Atmos Chem Phys Discuss **5**, 3561–3593 (2006)

Castro, L.M., Pio, C.A., Harrison, R.M., Smith, D.J.T.: Carbonaceous aerosol in urban and rural European atmospheres: estimation of secondary organic carbon concentrations. Atmos Environ **33**, 2771–2781 (1999)

Choi, J.K., Heo, J.B., Ban, S.J., Yi, S.M., Zoh, K.D., Source apportionment of PM2.5 at the coastal area in Korea. Sci Total Environ **447**, 370–380 (2013)

Chow, J.C., Watson, J.G., Chen, L.W.A., Arnott, W.P., Moosmuller, H.: Equivalence of elemental carbon by thermal/optical reflectance and transmittance with different temperature protocols. Environ Sci Technol **38**, 4414–4422 (2004)

Draxler, R.R., Rolph, G.D.: HYSPLIT (HYbrid Single-particle Lagrangian Integrated Trajectory) Model. Access via NOAA ARL READY website. NOAA Air Resources Laboratory, Silver Spring (2003). http://www.arl.noaa.gov/ready/hysplit4.html

Gupta, A.K., Karar, K., Srivastava, A.: Chemical mass balance source apportionment of PM10 and TSP in residential and industrial sites of an urban region of Kolkata, India. J Hazardous Materials **142**, 279–287 (2007)

Gadi, R., Shivani, Sharma, S.K., Mandal, T.K.: Source apportionment and health risk assessment of organic constituents in fine ambient aerosols ($PM_{2.5}$): a complete year study over National Capital Region of India Chemosphere **221,**583–596 (2019)

Gupta, S., Gadi, R., Mandal, T.K., Sharma, S.K.: Seasonal variations and source profile of n-alkanes in particulate matter (PM_{10}) at a heavy traffic site, Delhi. Environ Monit Assess **189**, 43 (2017)

Gupta, S., Gadi, R., Sharma, S.K., Mandal, T.K.: Characterization and source apportionment of organic compounds in PM10 using PCA and PMF at a traffic hotspot of Delhi. Sustain Cities Soc **39**, 52–67 (2018)

Hansen, J.M., Sato, R., Rued, L., Nazarenko, A., Lacis, G.A., Schmidt, G., Russell, I., Aleinov, M., Bauer, S., Bauer, N., Bell, B., Cairns, V., Canuto, M., Chandler, Y., Cheng, A., Del Genio, G., Faluvegi, E., Fleming, A., Friend, T., Hall, C., Jackman, M., Kelley, N.Y., Kiang, D., Koch, J., Lean, J., Lerner, K., Lo, S., Menon, R.L., Miller, P., Minnis, T., Novakov, V., Oinas, J.P., Perlwitz, J., Perlwitz, D., Rind, A., Romanou, D., Shindell, P., Stone, S., Sun, N., Tausnev, D., Thresher, B., Wielicki, T., Wong, M.Y., Zhang, X.: Efficacy of climate forcings. J Geophys Res **110**, D18104 (2005)

IPCC.: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp. (2013)

Jain, S., Sharma, S.K., Vijayan, N., Mandal, T.K.: Seasonal characteristics of aerosols ($PM_{2.5}$ and PM_{10}) and their source apportionment using PMF: A four year study over Delhi, India. Environ Poll **262**, 114337 (2020a)

Jain, S., Sharma, S.K., Choudhary, N., Masiwal, R., Saxena, M., Sharma, A., Mandal, T.K., Gupta, A., Gupta, N.C., Sharma, C.: Chemical characteristics and source apportionment of $PM_{2.5}$ using PCA/APCS, UNMIX, and PMF at an urban site of Delhi, India. Environ Sci Poll Res **24**(17), 14637–14656 (2017)

Jain, S., Sharma, S.K., Srivastava, M.K., Chaterjee, A., Singh, R.K., Saxena, M., Mandal, T.K.: Source apportionment of PM_{10} using receptor models in Indo-Gangetic plain (IGP) of India. Archives Environ Contamin Toxicol **76**, 114–128 (2019)

Jain, S., Sharma, S.K., Vijayan, N., Mandal, T.K.: Seasonal characteristics of aerosols ($PM_{2.5}$ and PM_{10}) and their source apportionment using PMF: A four year study over Delhi. India Environ Poll **262**, 114337 (2020b)

Jain, S., Sharma, S.K., Srivastava, M.K., Chatterjee, A., Vijayan, N., Tripathy, S.S., Kumari, K.M., Mandal, T.K., Sharma, C.: Chemical characterization, source apportionment and transport pathways of $PM_{2.5}$ and PM_{10} over Indo Gangetic Plain of India. Urban Clim **36**, 100805 (2021)

Kanakidou, M., Seinfeld, J.H., Pandis, S.N., Barnes, I., Dentener, F.J., Facchini, M.C., Dingenen, R.V., Ervens, B., Nenes, A.N.C.J.S.E., Nielsen, C.J., Swietlicki, E.: Organic aerosol and global climate modelling: a review. Atmos Chem Phy **5**(4), 1053–1123 (2005)

Kaushal, D., Kumar, A., Yadav, S., Tandon, A., Attri, A.K.: Wintertime carbonaceous aerosols over Dhauladhar region of North-Western Himalayas. Environ Sci Poll Res **25**, 8044–8056 (2018)

Khillare, P.S., Sarkar, S.: Airborne inhalable metals in residential areas of Delhi, India: distribution, source apportionment and health risks. Atmos Poll Res **3**(1), 46–54 (2012)

Kothai, P., Saradhi, I.V., Prathibha, P., Hopke, P.K., Pandit, G.G., Puranik, V.D.: Source apportionment of coarse and fine particulate matter at Navi Mumbai. India. Aerosol Air Qual Res **8**(4), 423–436 (2008)

Kulshrestha, A., Satsangi, P.G., Masih, J., Taneja, A.: Metal concentration of $PM_{2.5}$ and PM_{10} particles and seasonal variations in urban and rural environment of Agra, India. Sci Total Environ **407**(24), 6196–6204 (2009)

Kumar, A., Attri, A.K.: Biomass combustion a dominant source of carbonaceous aerosols in the ambient environment of western Himalayas. Aerosol Air Qual Res **16**(3), 519–529 (2016)

Kumar, A., Sarin, M.M.: Mineral aerosols from western India: temporal variability of course and fine atmospheric dust and elemental characteristics. Atmos Environ **43**, 4005–4013 (2009)

Lighty, J.S., Veranth, J.M., Sarofim, A.F.: Combustion aerosols: factors governing their size and composition implications to human health. J Air Waste Manag Assoc **50**(9), 1565–1618 (2000)

Lim, H.J., Turpin, B.J.: Origins of primary and secondary organic aerosol in Atlanta: Results of time-resolved measurements during the Atlanta supersite experiment. Environ Sci Technol **36**, 4489–4496 (2002)

Lim, Y.B., Tan, Y., Perri, M.J., Seitzinger, S.P., Turpin, B.J.: Aqueous chemistry and its role in secondary organic aerosol (SOA) formation. Atmos Chem Phys Discussions **10**(6), (2010)

Mandal, P., Sarkar, R., Mandal, A., Saud, T.: Seasonal variation and sources of aerosol pollution in Delhi. India. Environ Chem Lett **12**(4), 529–534 (2014)

McLennan, S.: Relationship between the trace element composition of sedimentary rocks and upper continental crust. Geochem Geophys Geosyst **2**, 1021 (2001). https://doi.org/10.1029/2000/GC000109

Morawska, L., Zhang, J.J.: Combustion sources of particles. Health Relevance and Source Signatures. Chemosphere **49**, 1045–1058 (2002)

Pant, P., Harrison, R.M.: Critical review of receptor modeling for particulate matter: a case study of India. Atmos Environ **49**, 1–12 (2012)

Perrino, C., Tiwari, S., Catrambone, M., Dalla Torre, S., Rantica, E., Canepari, S.: Chemical characterization of atmospheric PM in Delhi, India, during different periods of the year including Diwali festival. Atmospheric Pollut Res **2**(4), 418–427 (2011)

Pope, C.A., Ezzati, M., Dockery, D.W.: Fine-particulate air pollution and life expectancy in the United States. N. Engl. J. Med. **360**(4), 376–386 (2009a)

Pope, C.A., Ezzati, M., Dockery, D.W.: Fine-particulate air pollution and life expectancy in the United States. N Engl J Med **360**(4), 376–386 (2009b)

Rai, A., Mukherjee, S., Chatterjee, A., Choudhary, N., Kotnala, G., Mandal, T.K., Sharma, S.K.: Seasonal variation of OC, EC and WSOC of PM10 and their CWT analysis over the eastern Himalaya. Aerosol Sci Eng **4**, 26–40 (2020a)

Rai, P., Furger, M., El Haddad, I., Kumar, V., Wang, L., Singh, A., Dixit, K., Bhattu, D., Petit, J.E., Ganguly, D., Rastogi, N.: Real-time measurement and source apportionment of elements in Delhi's atmosphere. Sci Total Environ **742**:140332 (2020b)

Ram, K., Sarin, M.M.: Day–night variability of EC, OC, WSOC and inorganic ions in urban environment of Indo-Gangetic Plain: Implications to secondary aerosol formation. Atmos Environ **45**, 460–468 (2011)

Ramana, M.V., Ramanathan, V., Feng, Y., Yoon, S.C., Kim, S.W., Carmichael, G.R., Schauer, J.J.: Warming influenced by the ratio of black carbon to sulphate and the black-carbon source. Nat Geosci **3**, 542–545 (2010)

Ramgolam, K., Favez, O., Cachier, H., Gaudichet, A., Marano, F., Martinon, L.: Size-partitioning of an urban aerosol to identify particle determinants involved in the pro-inflammatory response induced in airway epithelial cells. Particle and Fibre Toxicology **6**(1), (2009).https://doi.org/10.1186/1743-8977-6-10

Rengarajan, R., Sarin, M.M., Sudheer, A.K.: Carbonaceous and inorganic species in atmospheric aerosols during wintertime over urban and high-altitude sites in North India. J Geophy Res **112**, D21307 (2007)

Robinson, A.L., Donahue, N.M., Shrivastava, M.K., Weitkamp, E.A., Sage, A.M., Grieshop, A.P., Pandis, S.N.: Rethinking organic aerosols: Semivolatile emissions and photochemical aging. Science **315**(5816), 1259–1262 (2007)

Salma, I., Chi, X.G., Maenhaut, W.: Elemental and organic carbon in urban canyon and background environments in Budapest, Hungary. Atmos Environ **38**, 2517–2528 (2004)

Sarin, M.M., Borole, D.V., Krishnaswami, S.: Geochemistry and geochronology of sediments from the Bay of Bengal and the equatorial Indian Ocean. Proc. Indian Academy of Science **88**, 131–154 (1979)

Sarkar, C., Chatterjee, A., Majumdar, D., Roy, A., Srivastava, A., Ghosh, S.K., Raha, S.: How the atmosphere over eastern Himalaya, India is polluted with carbonyl compounds? Temporal variability and identification of sources. Aerosol Air Qual Res **17**, 2206–2223 (2017)

Saxena, M., Sharma, A., Sen, A., Saxena, P., Saraswati, Mandal, T.K., Sharma, S.K.: Water soluble inorganic species of PM10 and PM2.5 at an urban site of Delhi, India: seasonal variability and sources. Atmos Res **184**, 112–125 (2017)

Sharma, S.K., Mandal, T.K., Dey, A.K., Deb, N., Jain, S., Saxena, M., Pal, S., Choudhuri, A.K., Yadav, S.: Carbonaceous and inorganic species in PM_{10} during wintertime over Giridih, Jharkhand (India). J Atmos Chem **75**, 219–233 (2018a)

Sharma, S.K., Mandal, T.K., Jain, S., Saraswati, S.A., Saxena, M.: Source apportionment of $PM_{2.5}$ in Delhi, India using PMF model. Environ Contam Toxicol **97**, 286–293 (2016)

Sharma, S.K., Mandal, T.K., Saxena, M., Sharma, A., Gautam, R.: Source apportionment of PM_{10} by using positive matrix factorization at an urban site of Delhi, India. Urban Climate **10**, 656–670 (2014a)

Sharma, S.K., Mandal, T.K., Sharma, C., Kuniyal, J.C., Joshi, R., Dhyani, P.P., Rohtash, Ghayas, H., Gupta, N.C., Sharma, P., Saxena, M., Sharma, A., Arya, B.C., Kumar, A.: Measurements of particulate ($PM_{2.5}$), BC and trace gases over the Northwestern Himalayan region of India. Mapan **29**(4), 243–253 (2014b)

Sharma, S.K., Mandal, T.K., Sharma, A., Saraswati, J.S.: Seasonal and annual trends of carbonaceous species of PM_{10} over a megacity Delhi, India during 2010–2017. J Atmos Chem **75**, 305–318 (2018b)

Sharma, S.K., Choudhary, N., Kotnala, G., Das, D., Mukherjee, S., Ghosh, A., Vijayan, N., Rai, A., Chatterjee, A., Mandal, T.K.: Wintertime carbonaceous species and trace metals in PM_{10} in Darjeeling: a high altitude town in the eastern Himalayas. Urban Climate **34**(4), 100668 (2020b)

Sharma, S.K., Choudhary, N., Srivastava, P., Naja, M., Vijayan, N., Kotnala, G., Mandal, T.K.: Variation of carbonaceous species and trace elements in PM_{10} at a mountain site in the central Himalayan region of India. J Atmos Chem **77**(3), 49–62 (2020b)

Shivani, Gadi, R., Sharma, S.K., Mandal, T.K.: Seasonal variation, source apportionment and source attributed health risk of fine carbonaceous aerosols over National Capital Region, India. Chemosphere **237**, 124500 (2019)

Shridhar, V., Khillare, P., Agarwal, T., Ray, S.: Metallic species in ambient particulate matter at rural and urban location of Delhi. J Hazard Mater **175**, 600–607 (2010)

Song, Y., Zhang, Y., Xie, S., Zeng, L., Zheng, M., Salmon, L.G., Shao, M., Slanina, S.: Source apportionment of $PM_{2.5}$ in Beijing by positive matrix factorization. Atmos Environ **40** (1), 526–1537 (2006)

Srinivas, B., Sarin, M.M.: $PM_{2.5}$, EC, and OC in an atmospheric outflow from the Indo-Gangetic Plain: temporal variability and aerosol organic carbon-to-organic mass conversion factor. Sci Total Environ **487**, 196–205 (2014)

Taylor, S.R., McLennan, S.M.: The geochemical evolution of the continental crust. Review of Geophysics **33**(2), 241–265 (1995)

Tiwari, S., Srivastava, A.K., Singh, A.K.: Heterogeneityin pre-monsoon aerosol characteristics over the Indo-Gangetic Basin.Atmos Environ **77**, 738-47 (2013)

Urban, N.B., Slifstein, M., Thompson, J.L., Xu, X., Girgis, R.R., Raheja, S., Haney, M., Abi-Dargham, A.: Dopamine release in chronic cannabis users: a [11c] raclopride positron emission tomography study. Biol. Psychiat. **71**(8), 677–683 (2012)

Viana, M., Kuhlbusch, T.A.J., Querol, X., Alastuey, A., Harrison, R.M., Hopke, P.K., Winiwarter, W., Vallius, M.: Source apportionment of particulate matter in Europe: a review of methods and results. J Aerosol Sci **39**, 827–849 (2008)

Watson, J.G., Chow, J.C., Frazier, C.A.: X-ray fluorescence analysis of ambient air samples. In: Landsberger S, Creatchman M (Eds.) Elemental Analysis of Airborne Particles. Gordon and Breach Science, Amsterdam **1**, 67–96 (1999)

WRP.: World Report of Population (2021). https://worldpopulationreview.com

Yin, J., Harrison, R.M., Chen, Q., Rutter, A., Schauer, J.J.: Source apportionment of fine particles at urban background and rural sites in the UK atmosphere. Atmos Environ **44**(6), 841–851 (2010)